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Some Practical Applications of Generalized Crystal-Structure Projections*

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The generalized projection of a periodic distribution $\varrho(x,y,z)$ is defined as $c\int_0^1 \varrho(x,y,z)\exp[2\pi iLz]dz$, and can be expressed as a two-dimensional Fourier series. Two practical applications of this function in X-ray analysis are described.

1. Generalized projection of a periodic distribution

Corresponding to the electron density

$$\varrho(x, y, z) = \frac{1}{V}\sum_{hkl} F(hkl)\exp[-2\pi i(hx+ky+lz)] \quad (1)$$

we define the generalized projection of this distribution on a plane perpendicular to the c axis as

$$\varrho_L(x, y) = c\int_0^1 \varrho(x, y, z)\exp[2\pi iLz]dz\,. \quad (2)$$

From (1), and the fact that

$$\begin{aligned}\int_0^1 \exp[2\pi i(L-l)z]dz &= 1 \text{ if } l = L\\ &= 0 \text{ if } l \neq L\,,\end{aligned}$$

we obtain

$$\varrho_L(x, y) = \frac{1}{A}\sum_{hk} F(hkL)\exp[-2\pi i(hx+ky)]\,. \quad (3)$$

This function was evaluated in the course of a crystal-structure analysis previously reported (Clews & Cochran, 1949), but its full significance was not realized at that time, although some use was made of it. Now with

$$F(hkL) = A(hkL)+iB(hkL)$$

and

$$\varrho_L(x, y) = C_L(x, y)+iS_L(x, y)\,, \quad (4)$$

we have from (3)

$$C_L(x, y) =$$

$$\frac{1}{A}\sum_{hk} A(hkL)\cos 2\pi(hx+ky)+B(hkL)\sin 2\pi(hx+ky)\,,$$

$$S_L(x, y) =$$

$$\frac{1}{A}\sum_{hk} B(hkL)\cos 2\pi(hx+ky)-A(hkL)\sin 2\pi(hx+ky)\,. \quad (5)$$

These functions assume simpler forms when the structure possesses symmetry. For example, for space group *Pmmm*,

$$C_L(x, y) = \frac{1}{A}\sum_{hk} F(hkL)\cos 2\pi hx\cos 2\pi ky\,,$$

and

$$S_L(x, y) = 0\,. \quad (6)$$

We now make use of the fact that when the distribution is composed of spherically symmetric atoms,

$$F(hkL) = \sum_{j=1}^{N} f_j(hkL)\exp[2\pi i(hx_j+ky_j+Lz_j)]\,. \quad (7)$$

Substituting in (3) and using (4) we obtain

$$C_L(x, y) = \sum_{j=1}^{N} \sigma_{jL}(x-x_j, y-y_j)\cos 2\pi Lz_j$$

and

$$S_L(x, y) = \sum_{j=1}^{N} \sigma_{jL}(x-x_j, y-y_j)\sin 2\pi Lz_j\,, \quad (8)$$

where

$$\sigma_{jL}(x, y) = \frac{1}{A}\sum_{hk} f_j(hkL)\exp[-2\pi i(hx+ky)]\,. \quad (9)$$

We see from (8) that $C_L(x, y)$ may be built up by multiplying each $\sigma_{jL}(x, y)$ by the factor $\cos 2\pi Lz_j$, and centering it at the point (x_j, y_j). Since $\sigma_{jL}(x, y)$ is circularly symmetric, it can be evaluated from the one-dimensional series

$$\sigma_{jL}(x, 0) = \frac{1}{A}\sum_{h}\{\sum_{k} f_j(hkL)\}\cos 2\pi hx\,. \quad (10)$$

2. Use of generalized projections in crystal-structure analysis

It often happens in practice that one projection of a crystal structure, say down the c axis, shows all atoms well resolved from one another. When this is the case, it is probable that the c axis is relatively short, and poor resolution will be obtained in all other projections. In such circumstances the functions $C_L(x, y)$ and $S_L(x, y)$ are valuable, as they possess the resolution of the c axis projection, but at the same time contain information about the atomic z co-

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* After this paper had been prepared for publication, an unusual and very neat application of generalized projections was reported by Raeuchle & Rundle (1952). These authors derive equation (3), but the second of their equations corresponding to our equations (5) appears to us to be incorrect. Thereafter the applications of the theory are different in the two papers; we have therefore submitted our paper without altering its form.

ordinates. Although they do not give this with the same degree of accuracy as a three-dimensional synthesis, fewer experimental data are required, the necessary coefficients all being obtainable from a set of Weissenberg photographs of a single layer line. Approximate phases must of course be determined from the known position of a heavy atom, or by calculation from a trial structure. Generalized projections can be refined in the same way as ordinary projections, the variables now being not the coordinates of the maxima (or minima), which we assume to have been determined from the corresponding projection, but their heights. From their heights in the final generalised projections; the values of $\begin{smallmatrix}\cos\\ \sin\end{smallmatrix}\, 2\pi L z_j$ can be determined.

Corresponding generalized Patterson projections may be useful in special circumstances (see for example Dyer, 1951*a*).

Generalized projections were found to be particularly useful in an investigation of the crystal structures of the compounds diglycylglycine ethyl ester hydrochloride and the corresponding hydrobromide (Dyer, 1951*b*). The compounds are closely isomorphous, the space group being *Pcab*. The projection of the electron density on (100), shown in Fig. 1, was obtained by the isomorphous-replacement method. In this projection the *c* axis is halved. Two molecules related by a glide plane at $y = \frac{1}{4}$, which appears as a line of symmetry in the projection, overlap and at first, of course, there was no way of telling which atom belonged to which molecule. The projection of the structure on (010) does not resolve this ambiguity, and in any case this projection could not be obtained by the isomorphous-replacement method because of the particular position (on $x = 0$) occupied by the replaceable atom. These difficulties were overcome by evaluating the function $C_1(y, z)$. Since the space group has a centre of symmetry, we have from (5)

$$C_1(y,z)=\frac{1}{A}\sum_{k=-\infty}^{+\infty}\sum_{l=-\infty}^{+\infty}F(1kl)\cos 2\pi(ky+lz)\,. \qquad (11)$$

From the relations between $F(1kl)$, $F(1\bar{k}l)$ etc. which are given by Lonsdale (1936) for this space group, we find

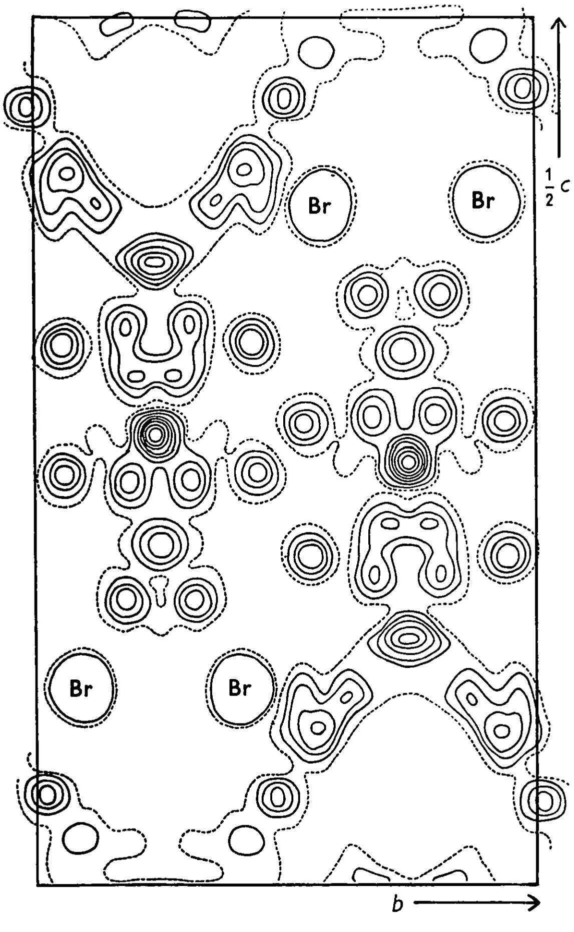

Fig. 1. Electron density in diglycylglycine ethyl ester hydrobromide, projected on (100).

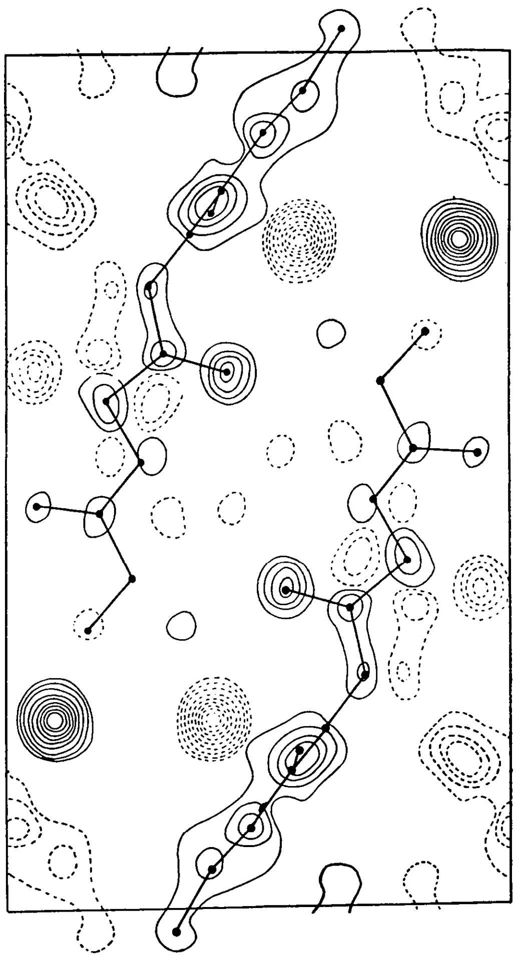

Fig. 2. Corresponding generalized projection for $H = 1$. Negative values of the function are indicated by broken contours.

$$C_1(y, z) = \frac{1}{A}\left\{2 \sum_{l=1}^{\infty} F(10l) \cos 2\pi lz + 4 \sum_{k=1}^{\infty} \sum_{l=1}^{\infty} F(1kl) \cos 2\pi ky \cos 2\pi lz\right\}_{k \text{ even},\ l \text{ odd}}$$
$$- \frac{1}{A}\left\{4 \sum_{k=1}^{\infty} \sum_{l=1}^{\infty} F(1kl) \sin 2\pi ky \sin 2\pi lz\right\}_{k \text{ odd},\ l \text{ odd}} . \qquad (12)$$

The signs of $F(1kl)$'s for l odd were determined by the isomorphous-replacement method, and $C_1(y, z)$ was evaluated for the bromine compound. The result is shown in Fig. 2. The lines of symmetry at $y = \frac{1}{4}$ and $\frac{3}{4}$ in Fig. 1 appear as lines of antisymmetry in Fig. 2. This follows from the fact that two atoms related by a glide plane at $y = \frac{1}{4}$ have coordinates (x, y, z) and $(x+\frac{1}{2}, \frac{1}{2}-y, z)$, so that the heights of the corresponding peaks in Fig. 2 depend on $\cos 2\pi x$ and $\cos 2\pi(x+\frac{1}{2})$; that is, they are equal in magnitude but opposite in sign. Two adjacent atoms p and q belonging to the same molecule will not differ greatly in their x coordinates, so that $\cos 2\pi x_p$ and $\cos 2\pi x_q$ will have the same sign, unless p and q lie on opposite sides of $x = \frac{1}{4}$ or $\frac{3}{4}$. Adjacent peaks in Fig. 2 which are both positive or both negative therefore usually represent atoms belonging to the same molecule. In this way it was proved that the atoms of one molecule are as shown in Fig. 2. Approximate x coordinates were obtained from the heights of the peaks in Fig. 2, and more accurately by inspection of the function $C_3(y, z)$. Finally, the signs of the $(h0l)$ structure factors were calculated, using the x coordinates obtained from the generalised projections, and the projection on (010) was evaluated.

3. Application of generalized projections to the calculation of structure factors

As an example, we consider a structure of symmetry *Pmmm*. Then, from (6),

$$F(hkL) = 4A \int_0^{\frac{1}{2}} \int_0^{\frac{1}{2}} C_L(x, y) \cos 2\pi hx \cos 2\pi ky \, dxdy . \qquad (13)$$

Corresponding expressions for $A(hkL)$ and $B(hkL)$ can be derived from (5) in the general case.

Now it may be shown that under certain conditions, which are fully explained in a paper by Sayre (1951), an integral such as (13) can be replaced by a summation, so that

$$F(hkL) = \frac{4A}{MN} \sum_{n=0}^{\frac{1}{2}N} \sum_{m=0}^{\frac{1}{2}M} C_L\left(\frac{n}{N}, \frac{m}{M}\right) \cos 2\pi \frac{nh}{N} \cos 2\pi \frac{mk}{M} . \qquad (14)$$

The practical steps in the use of this result are as follows:

(*a*) The functions σ_{jL} are calculated from (10) for each type of atom and for as many different values of L as are required. This is apt to be tedious; a considerable simplification results if the structure contains identical or similar (e.g. C, N and O) atoms. The scattering factor, multiplied by an appropriate temperature factor which is chosen so as to fulfill the conditions whereby (13) may be replaced by (14), can then be approximated by

$$f_j(hkL) = Z_j \exp\left[-(\pi^2/p)S^2\right], \quad \text{where} \quad S = 2 \sin \theta/\lambda ,$$

from which (Booth, 1946)

$$\sigma_{j0}(r) = Z_j(p/\pi) \exp\left[-pr^2\right] ,$$

where r is a distance measured from the origin, and hence

$$\sigma_{jL}(r) = \sigma_{j0}(r) \exp\left[-\pi^2 L^2/pc^2\right] ,$$

since $f_j(hkL) = f_j(hk0) \exp\left[-\pi^2L^2/pc^2\right]$ in this case.

σ_{jL} is then the same, apart from scale, for all atoms and for all values of L.

(*b*) The functions σ_{jL} are then multiplied by the appropriate values of $\cos 2\pi L z_j$, centered at the points (x_j, y_j), and 'sampled' on a lattice of spacing a/N, b/M to give the coefficients $C_L(n/N, m/M)$.

(*c*) The two-dimensional series is evaluated to give the $F(hkL)$'s.

By the use of this technique, a machine for the calculation of a two-dimensional series can be used to calculate general (hkl) structure factors. The method has been satisfactorily applied in practice, using punched-card equipment and on another occasion the electronic computer X-RAC (Pepinsky, 1947).

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